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# The *matlockite*-type praseodymium(III) oxide bromide PrOBr

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Key indicators: single-crystal X-ray study; $T$ = 293 K; mean $\sigma$(Pr–Br) = 0.001 Å; $R$ factor = 0.026; $wR$ factor = 0.059; data-to-parameter ratio = 11.3.

The crystal structure of the praseodymium(III) oxide bromide, PrOBr, can be best described with layers of agglomerated square antiprisms $[PrO_4Br_4]^{9-}$. These slabs are stacked along the *c* axis and linked *via* two different secondary contacts between $Pr^{3+}$ and $Br^-$. The $Pr^{3+}$ cations occupy the Wyckoff site 2*c* with 4*mm* symmetry and carry four $O^{2-}$ anions as well as four primary $Br^-$ anions, yielding a coordination number of 8. While the $Br^-$ anions exhibit the same site symmetry as the $Pr^{3+}$ cations, the oxide anions are located at the Wyckoff position 2*a* with site symmetry $\overline{4}m2$ and have four $Pr^{3+}$ cations as neighbours, defining a tetrahedron.

## Related literature

For prototypic PbFCl (mineral name: *matlockite*), see: Nieuwenkamp & Bijvoet (1932) and for an early powder study, see: Mayer *et al.* (1965). For other PrO*X* structures, see: Baenziger *et al.* (1950) for *X* = F, Zachariasen (1949) for *X* = Cl, and Potapova *et al.* (1977) for *X* = I. For data used for a comparison of the unit-cell dimensions, see: Shannon (1976) for ionic radii and Biltz (1934) for volume increments. For a proper classification of primary and secondary contacts, see: *MAPLE* (Hoppe, 1975) and for the bond-valence method, see: Brown (2002). For a comparison of intended synthesis attempts, see: Mattausch & Simon (1996); Lulei (1998).

## Experimental

### *Crystal data*

PrOBr
$M_r$ = 236.82
Tetragonal, $P4/nmm$
$a$ = 4.0671 (3) Å
$c$ = 7.4669 (5) Å
$V$ = 123.51 (2) Å$^3$
$Z$ = 2
Mo $K\alpha$ radiation
$\mu$ = 35.52 mm$^{-1}$
$T$ = 293 K
0.11 × 0.07 × 0.02 mm

### *Data collection*

Bruker–Nonius KappaCCD diffractometer
Absorption correction: numerical (*X-SHAPE*; Stoe & Cie, 1999)
$T_{min}$ = 0.049, $T_{max}$ = 0.535
1621 measured reflections
113 independent reflections
111 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.082

### *Refinement*

$R[F^2 > 2\sigma(F^2)]$ = 0.026
$wR(F^2)$ = 0.059
$S$ = 1.20
113 reflections
10 parameters
$\Delta\rho_{max}$ = 1.14 e Å$^{-3}$
$\Delta\rho_{min}$ = −2.52 e Å$^{-3}$

**Table 1**
Selected bond lengths (Å).

| | | | | |
|---|---|---|---|---|
| Pr—O | 4× | 2.3496 (3) | Pr—Br | 3.6083 (14) |
| Pr—Br | 4× | 3.2457 (8) | Pr—Br | 3.8586 (14) |

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *SCALEPACK* and *DENZO* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FI2117).

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# supplementary materials

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# The *matlockite*-type praseodymium(III) oxide bromide PrOBr

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## Comment

With the exception of PrOF (Baenziger *et al.* 1950) all praseodymium(III) oxide halides of the general composition PrO*X* (*X* = Cl – I; Zachariasen 1949, Potapova *et al.* 1977) crystallize with the *matlockite*-type structure (Nieuwenkamp & Bijvoet, 1932). The tetragonal crystal structure of the here presented praseodymium(III) oxide bromide PrOBr can be best described with layers of agglomerated square antiprisms $[PrO_4Br_4]^{9-}$ ($d(Pr^{3+}–O^{2-})$ = 234.96 (4) pm, $d(Pr^{3+}–Br^{-})$ = 324.57 (8) pm, $d(Pr^{3+}\cdots Br^{-})$ = 360.8 (1) and 385.9 (1) pm; Figure 1). These slabs are stacked along the *c*-axis and linked via two different secondary contacts between $Pr^{3+}$ and $Br^{-}$ (Figure 2). According to the ionic radii ($r_{Cl}$ = 180 pm, $r_{Br}$ = 195 pm, $r_{I}$ = 220 pm; Shannon, 1976) of the halide anions involved the expansion of the unit-cell dimensions occurs in quite an usual range, but the *c*-axes become significantly longer than the *a*-axes (*a*-axes: from 405.3 pm to 408.6 pm; *c*-axes: from 679.9 pm to 916.2 pm) along the $Cl^{-}–Br^{-}–I^{-}$ track. The lattice parameters of single crystalline PrOBr (*a* = 406.71 pm, *c* = 746.69 pm) fit almost perfectly with that from a previous powder diffraction study (*a* = 407.1 pm, *c* = 748.7 pm; Mayer *et al.* 1965). Differences in the molar volumes of the PbFCl-type praseodymium(III) oxide halides ($V_m$(PrOCl) = 33.6 $cm^3$/mol, $V_m$(PrOBr) = 37.2 $cm^3$/mol, $V_m$(PrOI) = 46.1 $cm^3$/mol) correspond well with the differences of the molar volumes of the respective halide anions ($V_m(Cl^{-})$ = 16.3 $cm^3$/mol, $V_m(Br^{-})$ = 19.2 $cm^3$/mol, $V_m(I^{-})$ = 24.5 $cm^3$/mol; Biltz 1934). However, the $Pr^{3+}$ cations occupy the *Wyckoff* site 2*c* (symmetry: 4*mm*) and bond four $O^{2-}$ anions as well as four+*one*+*one* $Br^{-}$ anions ending up with a total coordination number of 8+*1*+*1* (Figure 1). While the $Br^{-}$ anions exhibit the same site symmetry as the $Pr^{3+}$ cations, the oxide anions are located at *Wyckoff* position 2*a* with the site symmetry $\bar{4}m2$. *Bond-Valence* and *MAPLE* calculations support the interpretation of one important ($d(Pr^{3+}\cdots Br^{-})$ = 360.8 (1) pm) and one less important secondary contact ($d(Pr^{3+}\cdots Br^{-})$ = 385.9 (1) pm): The valency and ECoN for the first bond amounts to values of about 0.08 (with $R_0$ = 267 pm, *b* = 37 pm; Brown, 2002) and 0.12 (Hoppe, 1975), but almost *nil* for the second one, since this next nearest contact to bromide has only very low influence on the effective coordination sphere of the $Pr^{3+}$ cations (ECoN = 0.03).

## Experimental

Pale green, transparent, plate-shaped single crystals of PrOBr were obtained as by-product from a mixture of 0.06 g Pr, 0.38 g $PrBr_3$ and 0.01 g $NaN_3$, along with 0.30 g NaBr added as a flux. The mixture was kept at 800 °C for 7 days in an evacuated, sealed fused-silica vessel designed to produce the praseodymium(III) nitride bromide $Pr_3NBr_6$ in analogy with $La_3NBr_6$ (Lulei, 1998) and $Ce_3NBr_6$ (Mattausch & Simon, 1996).

## Refinement

The highest peak and the deepest hole in the final difference Fourier map are 95 pm and 84 pm apart from Pr.

## Figures

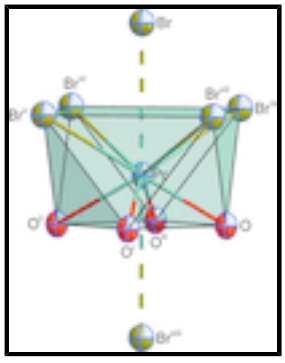

Fig. 1. View at the square antiprism $[PrO_4Br_4]^{9-}$ with two different $Br^-$ caps in *matlockite*-type PrOBr. Displacement ellipsoids are drawn at 90 % probability level. Symmetry codes: (i) -*x*+1, -*y*, -*z*; (ii) *x*-1, *y*, *z*; (iii) -*x*+1, -*y*+1, -*z*; (iv) -*x*+1, -*y*+1, -*z*+1; (v) -*x*, -*y*, -*z*+1; (vi) -*x*, -*y*+1, -*z*+1; (vii) -*x*+1, -*y*, -*z*+1; (viii) *x*, *y*, *z*-1.

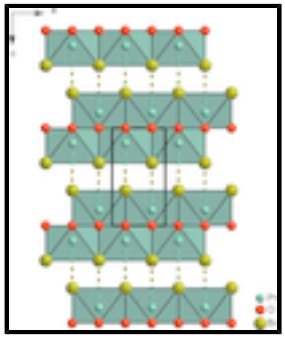

Fig. 2. Polyhedral representation of the *matlockite*-type PrOBr structure (dotted lines indicate the first of the two kinds of secondary contacts between $Pr^{3+}$ and $Br^-$).

## Praseodymium(III) oxide bromide

*Crystal data*

| | |
|---|---|
| PrBrO | $D_x$ = 6.368 Mg m$^{-3}$ |
| $M_r$ = 236.82 | Mo *K*α radiation, λ = 0.71069 Å |
| Tetragonal, *P*4/*nmm* | Cell parameters from 3957 reflections |
| Hall symbol: -P 4a 2a | θ = 0.4–27.9° |
| *a* = 4.0671 (3) Å | μ = 35.52 mm$^{-1}$ |
| *c* = 7.4669 (5) Å | *T* = 293 K |
| *V* = 123.51 (2) Å$^3$ | Plate, pale green |
| *Z* = 2 | 0.11 × 0.07 × 0.02 mm |
| *F*(000) = 204 | |

*Data collection*

| | |
|---|---|
| Bruker–Nonius KappaCCD diffractometer | 113 independent reflections |
| Radiation source: fine-focus sealed tube | 111 reflections with $I > 2\sigma(I)$ |
| graphite | $R_{int}$ = 0.082 |
| ω and φ scans | $\theta_{max}$ = 27.9°, $\theta_{min}$ = 5.5° |
| Absorption correction: numerical (*X-SHAPE*; Stoe & Cie, 1999) | *h* = −5→5 |
| $T_{min}$ = 0.049, $T_{max}$ = 0.535 | *k* = −5→5 |

| | |
|---|---|
| 1621 measured reflections | $l = -9 \rightarrow 9$ |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Primary atom site location: structure-invariant direct methods |
| Least-squares matrix: full | Secondary atom site location: difference Fourier map |
| $R[F^2 > 2\sigma(F^2)] = 0.026$ | $w = 1/[\sigma^2(F_o^2) + (0.0378P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| $wR(F^2) = 0.059$ | $(\Delta/\sigma)_{max} < 0.001$ |
| $S = 1.20$ | $\Delta\rho_{max} = 1.14$ e Å$^{-3}$ |
| 113 reflections | $\Delta\rho_{min} = -2.52$ e Å$^{-3}$ |
| 10 parameters | Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$ |
| 0 restraints | Extinction coefficient: 0.032 (5) |

*Special details*

**Geometry**. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

**Refinement**. Refinement of $F^2$ against ALL reflections. The weighted R-factor wR and goodness of fit S are based on $F^2$, conventional R-factors R are based on F, with F set to zero for negative $F^2$. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on $F^2$ are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å$^2$)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Pr | 0.2500 | 0.2500 | 0.15763 (8) | 0.0106 (4) |
| O | 0.7500 | 0.2500 | 0.0000 | 0.0129 (13) |
| Br | 0.2500 | 0.2500 | 0.64087 (17) | 0.0153 (4) |

*Atomic displacement parameters (Å$^2$)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Pr | 0.0084 (4) | 0.0084 (4) | 0.0148 (6) | 0.000 | 0.000 | 0.000 |
| O | 0.0114 (17) | 0.0114 (17) | 0.016 (3) | 0.000 | 0.000 | 0.000 |
| Br | 0.0149 (5) | 0.0149 (5) | 0.0160 (7) | 0.000 | 0.000 | 0.000 |

*Geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| Pr—O$^{i}$ | 2.3496 (3) | Pr—Pr$^{i}$ | 3.7165 (8) |
| Pr—O$^{ii}$ | 2.3496 (3) | Pr—Pr$^{x}$ | 3.7165 (8) |
| Pr—O$^{iii}$ | 2.3496 (3) | Pr—Pr$^{iii}$ | 3.7165 (8) |

| | | | |
|---|---|---|---|
| Pr—O | 2.3496 (3) | O—Pr$^{i}$ | 2.3496 (3) |
| Pr—Br$^{iv}$ | 3.2457 (8) | O—Pr$^{xi}$ | 2.3496 (3) |
| Pr—Br$^{v}$ | 3.2457 (8) | O—Pr$^{iii}$ | 2.3496 (3) |
| Pr—Br$^{vi}$ | 3.2457 (8) | Br—Pr$^{iv}$ | 3.2457 (8) |
| Pr—Br$^{vii}$ | 3.2457 (8) | Br—Pr$^{v}$ | 3.2457 (8) |
| Pr—Br | 3.6083 (14) | Br—Pr$^{vii}$ | 3.2457 (8) |
| Pr—Br$^{viii}$ | 3.8586 (14) | Br—Pr$^{vi}$ | 3.2457 (8) |
| Pr—Pr$^{ix}$ | 3.7165 (8) | | |
| O$^{i}$—Pr—O$^{ii}$ | 75.466 (11) | O—Pr—Pr$^{i}$ | 37.733 (6) |
| O$^{i}$—Pr—O$^{iii}$ | 119.87 (3) | Br$^{iv}$—Pr—Pr$^{i}$ | 107.075 (12) |
| O$^{ii}$—Pr—O$^{iii}$ | 75.466 (11) | Br$^{v}$—Pr—Pr$^{i}$ | 107.075 (12) |
| O$^{i}$—Pr—O | 75.466 (11) | Br$^{vi}$—Pr—Pr$^{i}$ | 168.31 (4) |
| O$^{ii}$—Pr—O | 119.87 (3) | Br$^{vii}$—Pr—Pr$^{i}$ | 66.920 (18) |
| O$^{iii}$—Pr—O | 75.466 (11) | Pr$^{ix}$—Pr—Pr$^{i}$ | 66.346 (15) |
| O$^{i}$—Pr—Br$^{iv}$ | 140.758 (5) | O$^{i}$—Pr—Pr$^{x}$ | 98.99 (2) |
| O$^{ii}$—Pr—Br$^{iv}$ | 140.758 (5) | O$^{ii}$—Pr—Pr$^{x}$ | 37.733 (6) |
| O$^{iii}$—Pr—Br$^{iv}$ | 71.938 (15) | O$^{iii}$—Pr—Pr$^{x}$ | 37.733 (6) |
| O—Pr—Br$^{iv}$ | 71.938 (15) | O—Pr—Pr$^{x}$ | 98.99 (2) |
| O$^{i}$—Pr—Br$^{v}$ | 71.938 (15) | Br$^{iv}$—Pr—Pr$^{x}$ | 107.075 (12) |
| O$^{ii}$—Pr—Br$^{v}$ | 71.938 (15) | Br$^{v}$—Pr—Pr$^{x}$ | 107.075 (12) |
| O$^{iii}$—Pr—Br$^{v}$ | 140.758 (5) | Br$^{vi}$—Pr—Pr$^{x}$ | 66.920 (18) |
| O—Pr—Br$^{v}$ | 140.758 (5) | Br$^{vii}$—Pr—Pr$^{x}$ | 168.31 (4) |
| Br$^{iv}$—Pr—Br$^{v}$ | 124.77 (5) | Pr$^{ix}$—Pr—Pr$^{x}$ | 66.346 (15) |
| O$^{i}$—Pr—Br$^{vi}$ | 140.758 (5) | Pr$^{i}$—Pr—Pr$^{x}$ | 101.39 (3) |
| O$^{ii}$—Pr—Br$^{vi}$ | 71.938 (15) | O$^{i}$—Pr—Pr$^{iii}$ | 98.99 (2) |
| O$^{iii}$—Pr—Br$^{vi}$ | 71.938 (15) | O$^{ii}$—Pr—Pr$^{iii}$ | 98.99 (2) |
| O—Pr—Br$^{vi}$ | 140.758 (5) | O$^{iii}$—Pr—Pr$^{iii}$ | 37.733 (6) |
| Br$^{iv}$—Pr—Br$^{vi}$ | 77.59 (2) | O—Pr—Pr$^{iii}$ | 37.733 (6) |
| Br$^{v}$—Pr—Br$^{vi}$ | 77.59 (2) | Br$^{iv}$—Pr—Pr$^{iii}$ | 66.920 (19) |
| O$^{i}$—Pr—Br$^{vii}$ | 71.938 (15) | Br$^{v}$—Pr—Pr$^{iii}$ | 168.31 (4) |
| O$^{ii}$—Pr—Br$^{vii}$ | 140.758 (5) | Br$^{vi}$—Pr—Pr$^{iii}$ | 107.075 (12) |
| O$^{iii}$—Pr—Br$^{vii}$ | 140.758 (6) | Br$^{vii}$—Pr—Pr$^{iii}$ | 107.075 (12) |
| O—Pr—Br$^{vii}$ | 71.938 (15) | Pr$^{ix}$—Pr—Pr$^{iii}$ | 101.39 (3) |
| Br$^{iv}$—Pr—Br$^{vii}$ | 77.59 (2) | Pr$^{i}$—Pr—Pr$^{iii}$ | 66.346 (15) |
| Br$^{v}$—Pr—Br$^{vii}$ | 77.59 (2) | Pr$^{x}$—Pr—Pr$^{iii}$ | 66.346 (15) |
| Br$^{vi}$—Pr—Br$^{vii}$ | 124.77 (5) | Pr—O—Pr$^{i}$ | 104.534 (11) |
| O$^{i}$—Pr—Pr$^{ix}$ | 37.733 (6) | Pr—O—Pr$^{xi}$ | 119.87 (3) |
| O$^{ii}$—Pr—Pr$^{ix}$ | 37.733 (6) | Pr$^{i}$—O—Pr$^{xi}$ | 104.534 (11) |
| O$^{iii}$—Pr—Pr$^{ix}$ | 98.99 (2) | Pr—O—Pr$^{iii}$ | 104.534 (11) |
| O—Pr—Pr$^{ix}$ | 98.99 (2) | Pr$^{i}$—O—Pr$^{iii}$ | 119.87 (3) |

| | | | |
|---|---|---|---|
| $Br^{iv}$—Pr—$Pr^{ix}$ | 168.31 (4) | $Pr^{xi}$—O—$Pr^{iii}$ | 104.534 (11) |
| $Br^{v}$—Pr—$Pr^{ix}$ | 66.920 (19) | $Pr^{iv}$—Br—$Pr^{v}$ | 124.77 (5) |
| $Br^{vi}$—Pr—$Pr^{ix}$ | 107.075 (12) | $Pr^{iv}$—Br—$Pr^{vii}$ | 77.59 (2) |
| $Br^{vii}$—Pr—$Pr^{ix}$ | 107.075 (12) | $Pr^{v}$—Br—$Pr^{vii}$ | 77.59 (2) |
| $O^{i}$—Pr—$Pr^{i}$ | 37.733 (6) | $Pr^{iv}$—Br—$Pr^{vi}$ | 77.59 (2) |
| $O^{ii}$—Pr—$Pr^{i}$ | 98.99 (2) | $Pr^{v}$—Br—$Pr^{vi}$ | 77.59 (2) |
| $O^{iii}$—Pr—$Pr^{i}$ | 98.99 (2) | $Pr^{vii}$—Br—$Pr^{vi}$ | 124.77 (5) |

Symmetry codes: (i) −*x*+1, −*y*, −*z*; (ii) *x*−1, *y*, *z*; (iii) −*x*+1, −*y*+1, −*z*; (iv) −*x*+1, −*y*+1, −*z*+1; (v) −*x*, −*y*, −*z*+1; (vi) −*x*, −*y*+1, −*z*+1; (vii) −*x*+1, −*y*, −*z*+1; (viii) *x*, *y*, *z*−1; (ix) −*x*, −*y*, −*z*; (x) −*x*, −*y*+1, −*z*; (xi) *x*+1, *y*, *z*.

**Fig. 1**

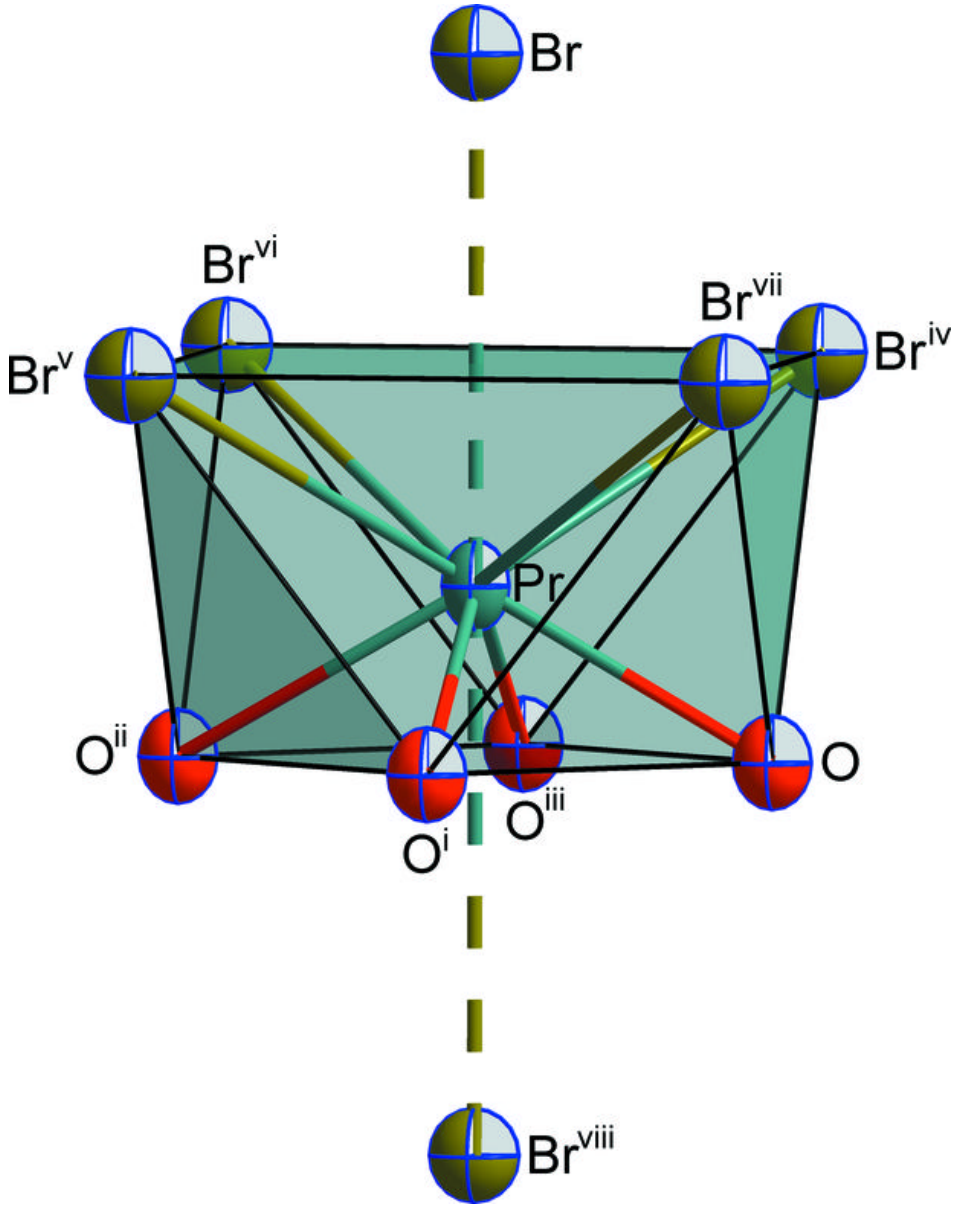
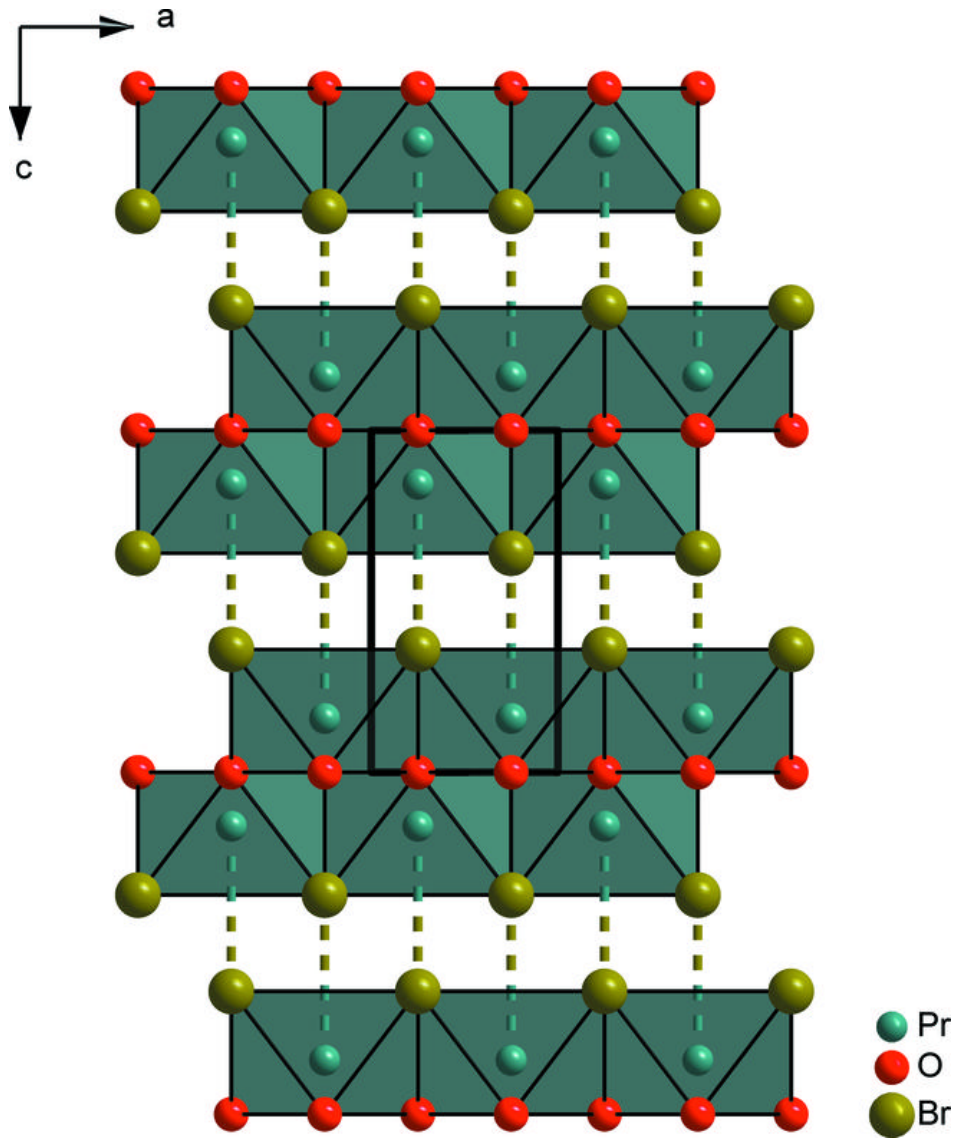
Fig. 2